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TITLE MAGNETISM AND BONDING IN ACTINIDE AND RARE EARTH SYSTEMS

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Magnetism and Bonding in Actinide and Rare Earth systems (INVITED)

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ABSTRACT:

The importance of including all of Hund's rules in self consistent electronic structure calculations is pointed out. We present a scheme that accounts for the interactions that lead to these rules, and we give examples of when these interactions become important. Calculated ground state properties (chemical bonding, magnetic moment, magnetic form factor) of actinide and rare earth systems are found to agree better with experiment when all Hund's rules are accounted for. On the other hand, for Fe, Co and Ni we find that it is a reasonable approximation to neglect Hund's second and third rule.

I INTRODUCTION

The nature of the f electrons and their contribution to magnetism and cohesion, in actinide and rare earth systems, has over the last two decades been studied thoroughly, both experimentally and theoretically. Early calculations for the light actinides showed that a 5f band was pinned at the Fermi level (E_F) and that the 5f electrons therefore must participate in the chemical bond.[1] The picture of delocalized, bonding 5f electrons in the light actinides was further strengthened by the fact that the calculated equation-of-state gave equilibrium volumes, bulk modulii and cohesive energies in good agreement with experiment.[2] The light actinides are therefore best described as having itinerant and bonding 5f electrons in a non spin-split 5f band, pinned at E_F. The formation of compounds can drive the 5f shell to become localized, and Hill pointed out that there exists a critical actinide-actinide distance for which there is an onset of magnetism.[3] However magnetism is not allways equivalent to localization, the 3d metals (Cr-Ni) is a good example of itinerant magnetism. Therefore the finding of magnetism in actinide systems cannot be taken as a unike signal of localization. For instance, it was shown that the magnetism in UNi_2 is due to itinerant, spin polarized 5f electrons.[4] The magnetic properties of UNi_2 were furthermore found to be highly unusual, since it was discovered, for the first time ever, that itinerant 5f electrons can have a large orbital moment accompanying the spin moment. Perhaps the best way to meassure spin and orbital moments is with neutrons and since the discovery of the unique magnetic properties of UNi_2, more actinide systems have been detected to show similar properties (for instance UFe_2 [5] and $PuFe_2$ [6]).

On the theoretical side, the necessity of treating all realtivistic effects (including the spin-orbit coupling) was shown by Brooks et al.[7], who calculated the magnetic moments and the magnetic form factor of UN. Here it was shown that the anomalous shape of the meassured uranium form factor could be reproduced in the calculations, only when the spin-orbit spliting was included in the band Hamiltonian.

Hence, as shown in refs. 4-7 neither spin nor orbital moments can be taken as being unique to localization. Similar work was done on other narrow band systems, and it was found that the formalism described in ref.7 reproduced the magnetic moments of $NpSn_3$ [8] and UCu_5 [9]. Lately we have persued in attempts to calculated the magnetic properties of actinide and rare earth systems, using the local spin density approximation (LSDA) and treting the spin-orbit coupling explicitly. For some systems this seems to give reasonable results (for instance UN and UFe_2), but it has been pointed out that additional terms, describing Hund's second rule correlations[10], has to be treated in theories attempting to describe magnetism and cohesion in narrow band systems. A slightly modified version of the orbital polarization formalism (Hund's second rule) described in ref.10, has been used on a number of systems yielding cohesive and magnetic properties in good agreement with experiment.[11] Below we will review some of these results together with some more recent work. The rest of this paper is organized as follows. Section II describes the magnetic properties of some selected actinide systems and it is shown that the onset of magnetism can be explained using a modified Stoner theory. The computational aspects of this work are briefly described in section III and in section IV we show calculated results for some selected actinide systems. The results for some selected rare earth systems are presented in section V and section VI offers some conlusions.

II Magnetic properties of selected actinide systems

The magnetic properties of actinide systems are unusual from many aspects. For instance, in an isostructural series of compounds involving actinides which are known to have delocalized 5f electrons (an example are UIr_2, $NpIr_2$ and $PuIr_2$) one would intuit veley expect the magnetic properties to change across the series in a regular pattern. It is for instance expected that since $NpIr_2$ has narrower 5f bands than UIr_2, therefore should show an increased tendency towards magnetism. This is indeed the case, since UIr_2 is a paramagnet and $NpIr_2$ orders in an antiferromagnetic structure. Contrary to these argu-

ments $PuIr_2$ does not order magnetically, but is insted a normal temperature independent paramagnet. Many Pu compounds show the same puzzling behaviour. The onset of magnetism is normally studied using the Stoner theory. For actinides, where relativistic effects are important, a slightly modified theory has to be used which accounts for these effects. The relativistic Stoner criterion for the onset of ferromagnetism has been shown to be of the form:[12]

$$I \bullet {D_R}^T \geq 1 \tag{1}$$

where ${D_R}^T$ is:

$${D_R}^T = \Sigma_t n_t \Sigma_l{}' D_{tl} + n_{An} D_R \tag{2}$$

The prime inicates that the summation should exclude the actinide 5f states and D_{tl} is the DOS at E_F for orbital (t,l), n_t is the number of atoms of type t, n_{An} is the number of actinide atoms and D_R is:

$$D_R = \Sigma_j \Sigma_{m_j<0} D_{j,m_j} ((C_+{}^{j,m_j})^2 - (C_-{}^{j,m_j})^2) \tag{3}$$

Furthermore, I is a generalized Stoner exchange parameter:

$$I = \Sigma_t n_t \Sigma_l{}' (\frac{D_{tl}}{{D_R}^T})^2 J_{tl} + n_{An} (\frac{D_R}{{D_R}^T})^2 J_{Anf} \tag{4}$$

with J_{tl} being the exchange integral of the orbital (t,l)[13]. We show in Table.1 the relativistic Stoner product for some selcted actinide systems. Notice that Eqn.1 accurately accounts for when there is magnetic ordering. The reason for the absence of magnetic ordering in many Pu compounds is shown in Fig.1, where we plot our calculated density of

states (DOS) for $PuIr_2$. Notice that E_F is located in the dip between the $5f_{5/2}$ and $5f_{7/2}$ partial DOS and the total DOS at E_F is therefore quite low. Since this quantity enters Eqs.1-4, it becomes clear why many Pu systems show lack of magnetic ordering. The spin-orbit coupling also quenches the spin movement, since as seen from Eqn.3 the spin projection involves the Clebsh-Gordan coefficients. This spin projection is always smaller than one, reducing the value of D_R and D_R^T compared to a nonrelativistic theory.

However, notice in Table.1 that $PuFe_2$ does order magnetically and therefore is unusual in comparison to other Pu systems. In this system it is the Fe atom that drive the magnetic transition,[14] irrespective of the Pu atom. As a matter of fact, for the same reson UFe_2 and $NpFe_2$ orders ferromagnetically as well.

III Details of the calculations

The calculated magnetic properties of some selected actinide systems will be discussed in the next section. The calculations were performed using the linear muffin-tin orbitals method (LMTO)[15], with the combined correction terms. The spin-orbit coupling was included at each variational step.[15] In addition we also included the orbital polarization, using the formalism suggested in ref.11. Therefore an orbital with azimuthal and magnetic quantum number (l,m_l) was shifted by E^3Lm_l. L is the orbital moment and E^3 is the Racah parameter[16] of the f electrons (when we deal with d electrons the Racah parameter is denoted B). This was done for each spin chanel, i.e. we have supressed a spin index for all the quantities above. The total orbital moment was then calculated as the sum of the spin up and down contributions, i.e. $L = \Sigma_\sigma L_\sigma$. All calculations were carried out until they were self consistent with changes of the order of 0.1% in spin and orbital moments, between consecutive iterations. The calculations were furthermore sampled at not less than 45 k-points in the irreducible wedge of the Brillouin zone (the exact number of k-point depending on the crystal structure in question). The Bart-Hedin[17] and Vosko-Wilk-Nusair[17] parametrizations were used in the generation of the potential. Since we

found very litle difference between them we will not specify for which system we used which specific parametrization.

IV Actinide systems

The calculated magnetic moments, located on the actinide atom, are listed together with experimental data in Table.2. Notice that the calculated moments are obtained from two levels of approximation, i.e. normal spin polarized calculations and calculations treating all Hund's rules. As seen, normal spin-polarized energy band calculations cannot account for the experimental data. On the other hand the calculations that involve all Hund's rules give results in good agreement. The theoretical moments given in Table.2, are also decomposed to spin and orbital contributions. In all the studied systems we find an orbital moment which is larger than and antiparalell to the spin moment. This is consistent with Hund's second rule, which states that for less than half filled shells the spin and orbital moments should be antiparalell. The ratio of the orbital and total moment, denoted C_2, is also compared with experimental values in Table.2. Notice that the C_2 value ranges from 1-23, depending on the system and that theory and experiment agree qualitativeley. The values of C_2 will determine the shape of the magnetic form factor and in Fig.2 and Fig.3 we give examples of two extreme cases; UNiSn(C_2=1) and UFe_2 (C_2=23). The calculated formfactors are seen to be very different. The reason for the difference between the two can be seen from the expression for the magnetic form factor (in the dipole approximation):[18]

$$\mu F(Q) = \mu(< J_0 > + C_2 < J_2 >) \tag{5}$$

The functions $< J_0 >$ and $< J_2 >$ are sperical averages of Bessel functions and they can easily be calculated from the charge and spin density of a specific atomic site. μ is the total magnetic moment of the atomic site in question and Q is the momentum transfer.

In Fig.4 we show as an example, for UNiSn, $< J_0 >$ and $< J_2 >$. Their shape is very different, and depending on the value of C_2 their weighted sum, i.e. the total form factor, will also be very different. Meassurements of UNiSn[19] and UFe_2 [5] show formfactors that qualitativeley agree with our data, with the same shape as for the data shown in Fig.2 and 3. For UFe_2 it seems that our calculated formfactor deviates most from experiments,[5] which show smaller values of the meassureed form factors compared to our calculated data. We believe that the analysis of neutron scattering experiments should preferably be made using $< J_0 >$ and $< J_2 >$ functions which are calculated from the spin density of the specific system in question. The discrepancy between theory and experiment in UFe_2 will probably remain, even if the analysis of the experimental data is refined, and furter studies of this system are desired.

V Rare earth systems

We show the calculated equation-of-state, spin and orbital moments for Ce in Fig.5. These results were obtained from calculations invoking all Hund's rules. Notice that for large volumes the ground state has a spin moment of $\sim 1\mu_B$ and an orbital moment of $\sim -3\mu_B$. These values reflect the fact that the the m_l=-3,$\sigma = 1/2$ subband pushed below E_F, whereas all the other 4f subbands are virtually empty. Almost all of the 4f contribution to the bonding is therefore lost. With increasing pressure the 4f band becommes broader and Hund's rules correlations suppressed. At a volume corresponding to the volume of γ-Ce, we obtain a van der Waals loop in the equation-of-state and both the spin and orbital moments are lost in this process. A Maxwell equal area costruction gives a volume collaps in good agreement with what has been observed experimentally for Ce. In Table.3 we list the calculated and experimental ground state properties of γ- and α-Ce , togehter with those for Pr and Nd. The agreement between experiment and theory is good. γ-Ce , Pr and Nd are all characterised by having 1,2 and 3 4f subbands pushed below E_F, respectiveley, with the other 4f subbands empty. This shows that it is quite possible to

describe localized states within a band picture, since filled bands in a Block representation is identical to a localized, Wannier orbital representation.

VI Conclusion

We have given examples of systems where, for an accurate desribtion of the electronic structure and the ground state properties, it is nessecary to treat all hund's rules. When treating these Hund's rules, according to ref.11, good agreement between theory and experiment is found for the systems studied. A similar treatment of the Mott insulator CoO gave good agreement between theory and experiment[20], showing that Hund's rules correlations are not constrained to f electron systems.

We have shown that, when treating all Hund's rules, it is quite possible to calculate the electronic structure and related properties for systems having orbitals with various degrees of localization or itinerancy. For instance, we find it accurate to treat the electronic structure of both α- and γ-Ce within exactly the same formalism, although the 4f electrons are itinerant in one system and localized in the other. An alternative would be to choose the 4f states of γ-Ce to be localized, by putting them in the core, and essentially solving an atomic problem. However this approximation does not have the flexibility for the system to determine which ground state that minimizes the total energy (localized or itinerant). We believ that the main advantage with our formalism is that the system indeed does have this flexibility.

Finally it is worthwhile to notice that the above described orbital polarizartion corrections do not have a dramatic influence on the electronic structure or the magnetic moments of systems for which LSDA is known to reproduce experiments. Nameley, our orbitally polarized calculations give essentially the same results as conventional spin polarized electronic structure calculations for Fe, Co and Ni.

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Table 1

Relativistic Stoner products and type of ordering for selected actinide systems

System	Stoner product	Type of ordering
$PuFe_2$	1.4	ferro
$PuCo_2$	0.9	para
$PuNi_2$	0.5	para
$PuIr_2$	0.6	para
Pu	0.3	para
Np	0.3	para

Table 2

Theoretical and experimental data for the spin and orbital moments of some selected actinide systems. The theory values indicated with one asterisc were obtained from calculations invoking all Hund's rules and the theory values indicated with two asteriscs were obtained from normal spin polarized calculations.

System		total moment	spin moment	orbital moment	C_2
UFe_2	experiment	0.01	—	—	23
	*theory	0.05	-0.83	0.88	18
	**theory	-0.51	-0.51	—	—
$NpFe_2$	experiment	1.09	—	—	—
	*theory	1.20	-2.29	3.49	3
	**theory	-0.73	-0.73	—	—
$PuFe_2$	experiment	0.39	—	—	6
	*theory	0.33	-3.19	3.52	11
	**theory	-4.15	-4.15	—	—
$NpOs_2$	experiment	0.25-0.44	—	—	—
	*theory	0.50	-2.57	3.07	6
	**theory	2.98	2.98	—	—
$NpAl_2$	experiment	1.5	—	—	—
	theory	1.30	-3.20	4.50	4
	**theory	3.56	3.56	—	—
$NpCo_2$	experiment	1.1	2.2	3.3	25 ~~25~~
	*theory	1.30	-3.20	4.50	4
	**theory	3.56	3.56	—	—
UCoAl	experiment	0.30	—	—	—
	*theory	0.43	-0.59	1.02	2
	**theory	0.77	0.77	—	—
UNiSn	experiment	1.55	—	—	1.1
	*theory	1.88	-1.66	3.54	1.9
	**theory	1.99	1.99	—	—

Table 3

Ground state properties for Ce, Pr and Nd

	Ce	Pr	Nd
$V_{exp}(Å^3)$	(γ)34.3	34.5	34.2
	(α)29.4		
$V_{theor}(Å^3)$	(γ)34.4	34.0	33.5
	(α)28.8		
B_{exp}(kbar)	(γ)239	305	327
	(α)270		
B_{theor}(kbar)	(γ)220	345	371
	(α)260		

Figure Captions

Fig. 1. Calculated DOS for $PuIr_2$. E_f is at zero and is marked by a vertical line. Energies are in electron volts. The rrea which is hatched from left to righ represents the $5f_{5/2}$ partial DOS and the area wich is hatched from right to left represents the $5f_{7/2}$ partial DOS. The uper curve is the total DOS.

Fig. 2. Calculated uranium form factor of UNiSn.

Fig. 3. Calculated uranium form factor of UFe_2.

Fig. 4. Calculated $< J_0 >$ and $< J_2 >$ functions, for the uranium atom in UNiSn.

Fig. 5. Calculated equation-of-state (lower panel), spin (midle panel) and orbital (uper panel) moment for Ce.

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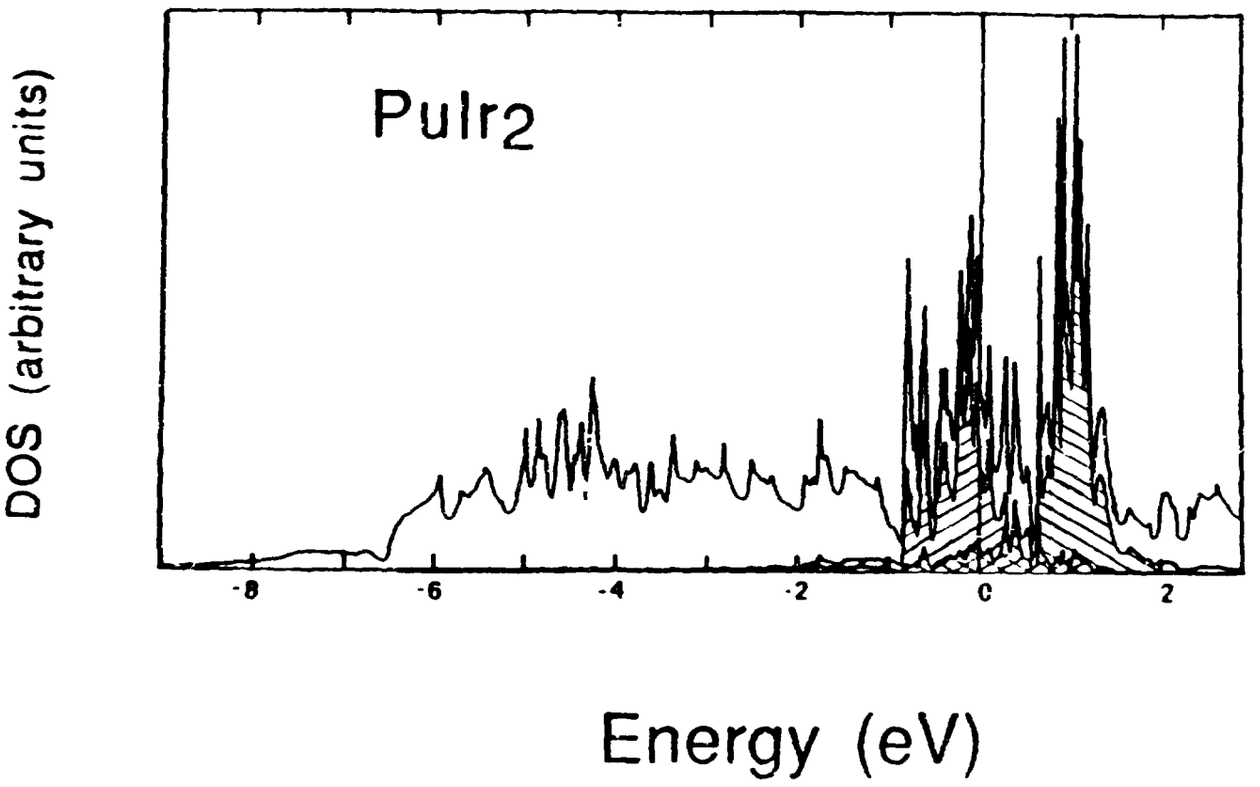
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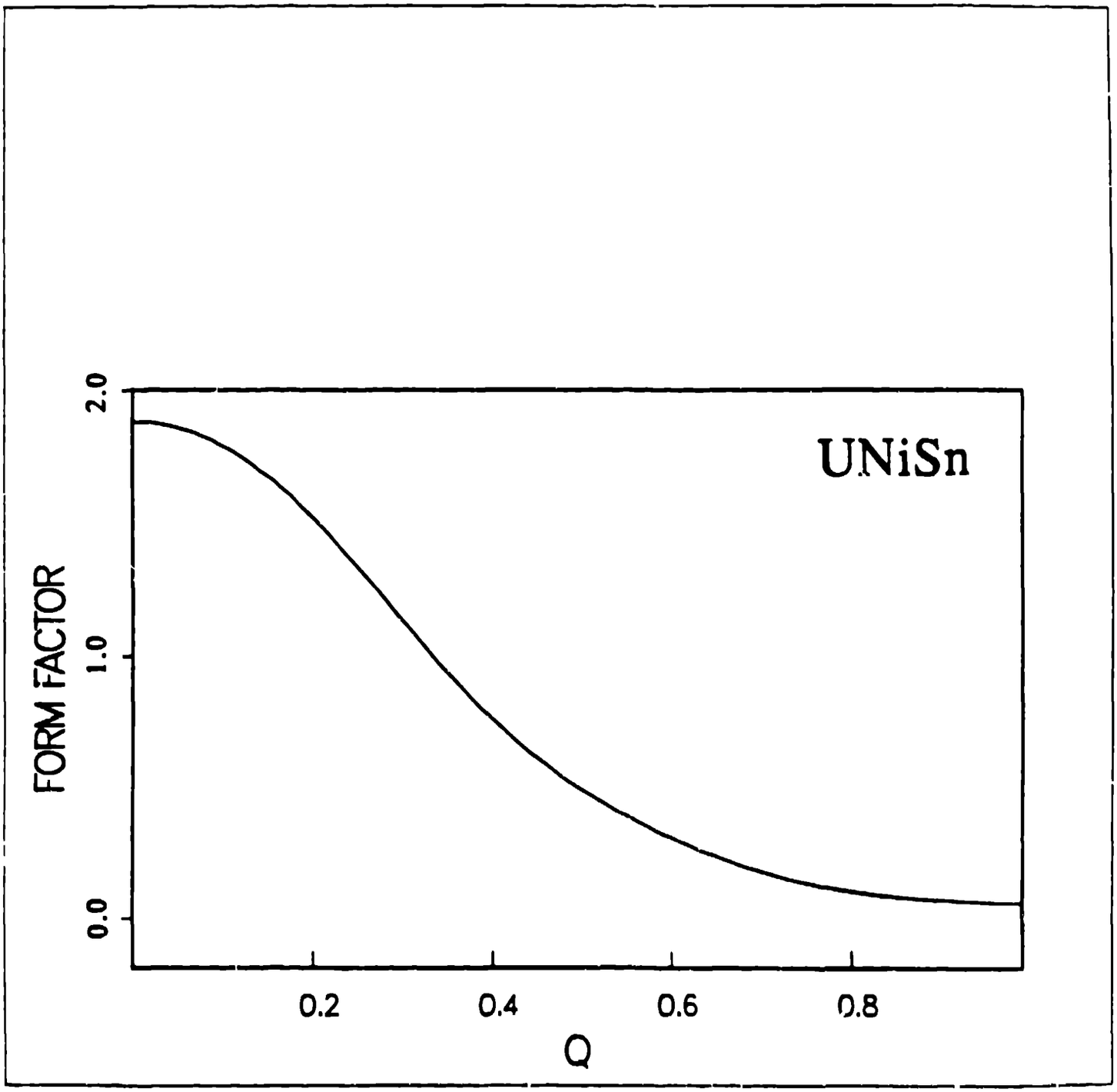
Energy (eV)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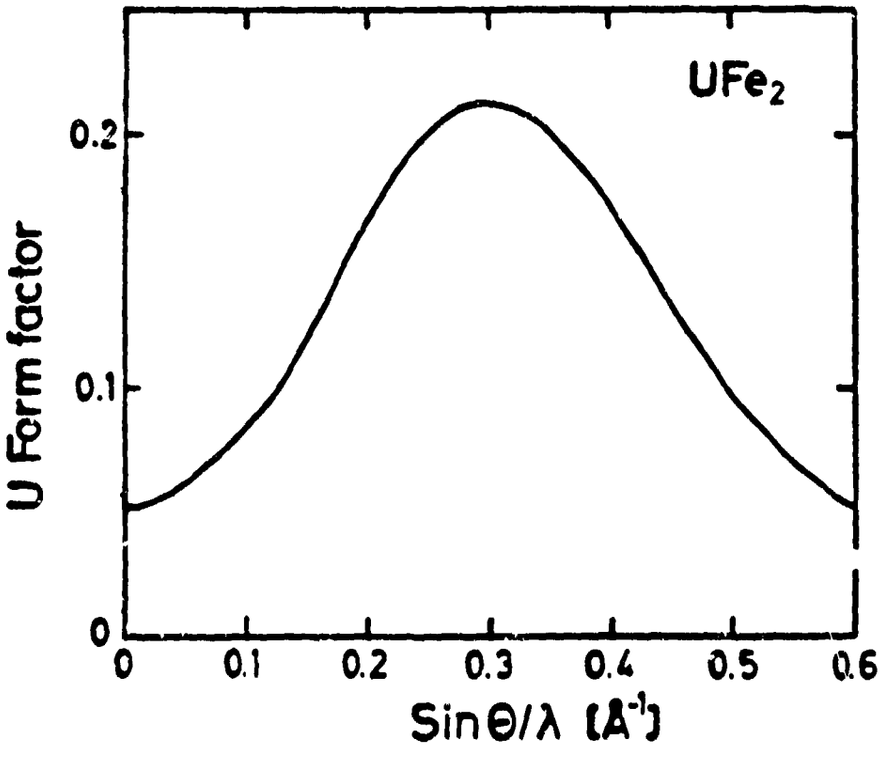
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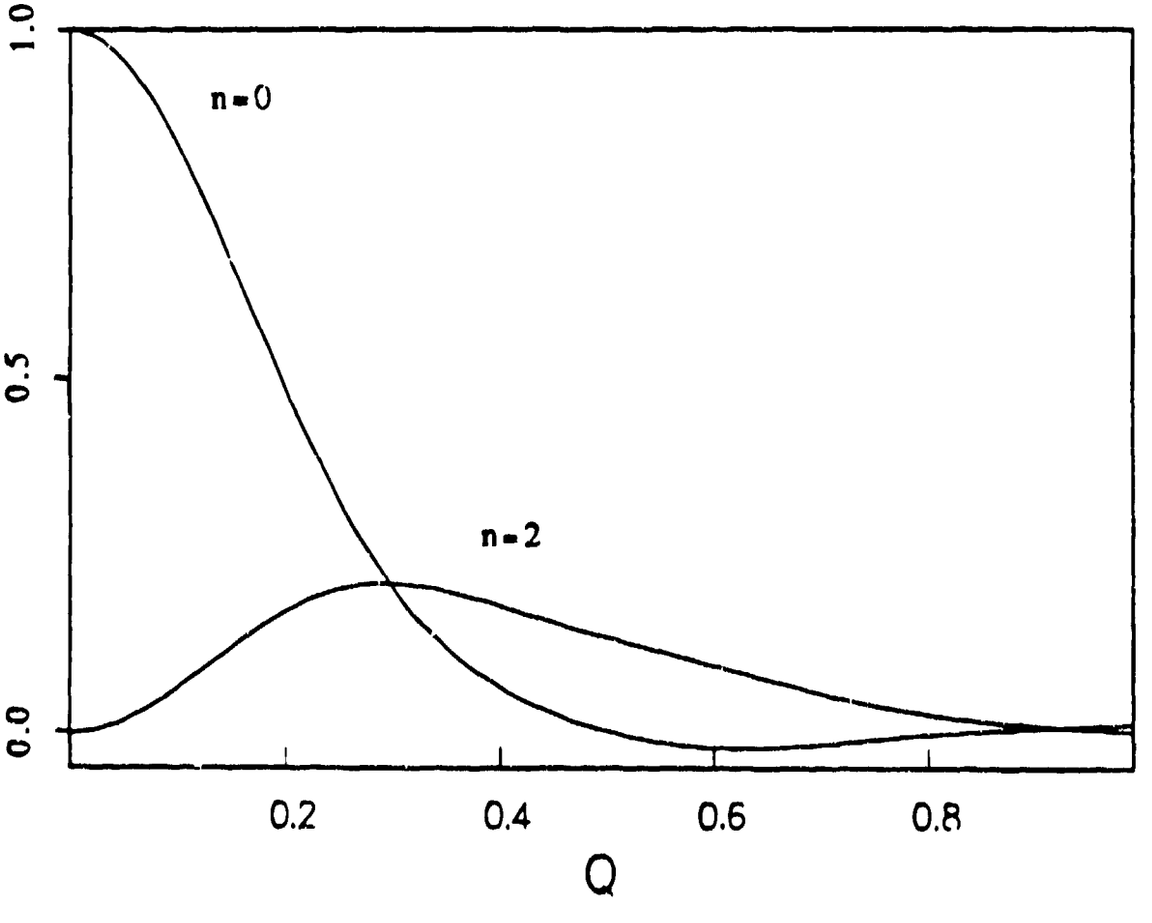
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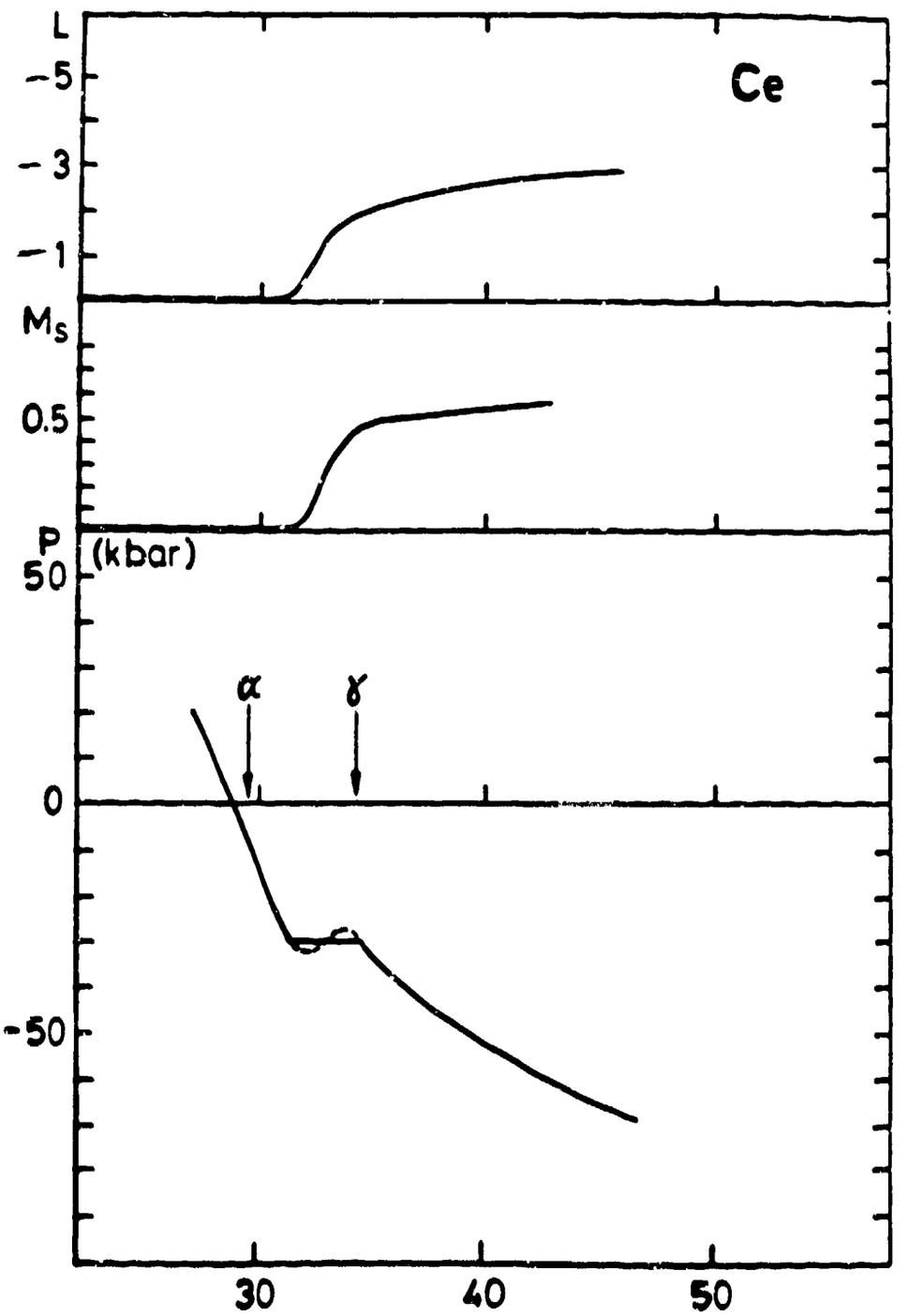
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